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Note

Synthesis of C_8 alkyl glycosides via palladium-catalyzed telomerization of butadiene with O-benzylated aldoses

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Abstract—Conditions of the butadiene telomerization with benzylated aldoses with a free anomeric hydroxyl, which efficiently furnish the corresponding octadienyl compounds have been determined. Deprotection and hydrogenation of the telomers over Pd/C led to the octyl glycosides.

Keywords: Telomerization; Palladium; Benzylated aldoses hemiacetals; Octyl glycosides

In recent years, much attention has been focused on the use of alkyl glycosides derived from renewable carbohydrate raw materials as non-ionic surfactants.[1] Although a great number of preparative methods have been described,[2] developing new and economical routes to these compounds remains an important target. In this respect, the butadiene telomerization reaction carried out in the presence of free carbohydrates as telogens, constitutes an elegant alternative to the Fischer glycosylation.[3–7] The use of acetyl protected carbohydrates with a free anomeric hydroxyl group has allowed to reduce the number of isomers formed.[8] Since the benzyl protective group is commonly employed in carbohydrate chemistry, we wish to describe here the results of butadiene telomerization with benzylated sugars hemiacetals. We have also studied the hydrogenation–deprotection step allowing the one-pot transformation of the resulting telomers into C_8 alkyl glycosides.

Preliminary experiments were carried out at 75 °C in DMF, using 2,3,4-tri-*O*-benzyl-β-D-arabinofuranose (**1**), butadiene (15 equiv), 2% of $Pd(acac)_2/2PPh_3$ as the catalyst system in a 50 mL stainless steel autoclave. Only 38% conversion of **1** was observed after 2 h, affording 22% of the expected telomers **3** and **4**, in addition to 12% of lactone **5**‡ (Scheme 1; Table 1, entry 1). Increasing the reaction time to 18 h or the catalyst amount to 5 mol % did not significantly modify the results.

To increase the efficiency and the selectivity of the reaction, different conditions were then tested. Switching from DMF to THF led to slightly better yields of the telomers. The nature of Pd^{II} source ($Pd(acac)_2$, entry 2 or $Pd(OAc)_2$, entry 3) had no influence on the reaction. The results were improved and reasonable conversions observed by increasing the relative butadiene amount (30 equiv instead of 15 equiv). With 30 equiv of butadiene, the use of 2% or 5% of the palladium catalyst led to the desired telomers with similar yields, but lactone **5** was again isolated (entries 4 and 5). Lactone formation

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‡ The side oxidation reaction leading to the lactone did not proceed when free pentoses[6,7] or acetylated pentoses[8] were the substrates, but could become a synthetic pathway starting from benzylated pentoses, after an adjustment of the experimental conditions.[9]

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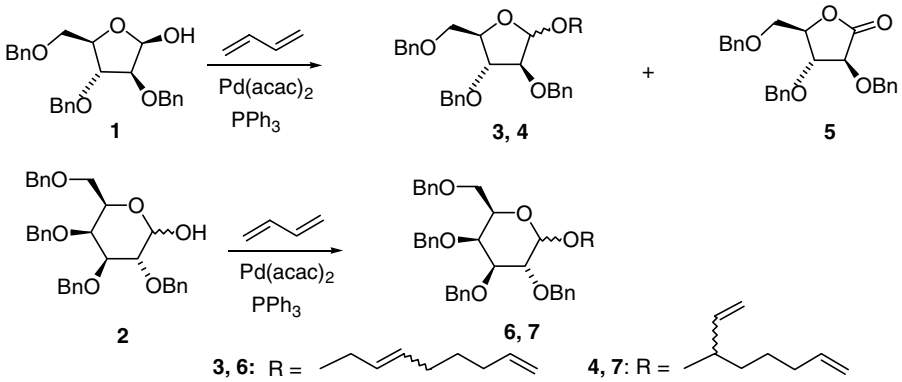


Scheme 1. Butadiene telomerization with O-benzylated furanose **1** and pyranose **2** derivatives.

Table 1. Palladium-catalyzed telomerization of butadiene with protected aldoses **1** and **2**[a]

Entry	Sugar	Pd (mol %)	C_4H_6 (equiv)	Solvent	Time (h)	Conv (%)	Products, yield[b] (%) (ratio[c])	
							3+**4** (**3**/**4**)	**5**
1	**1**	$Pd(acac)_2$ (2)	15	DMF	2	38	22 (4:1)	12
2	**1**	$Pd(acac)_2$ (2)	15	THF	18	56	36 (nd[e])	18
3	**1**	$Pd(OAc)_2$ (5)	15	THF	24	60	39 (nd[e])	22
4	**1**	$Pd(acac)_2$ (2)	30	THF	24	79	60 (4:1)	18
5	**1**	$Pd(acac)_2$ (5)	30	THF	24	82	63 (4:1)	19
6	**1**[d]	$Pd(acac)_2$ (5)	30	THF	24	57	5	50
7	**1**	$Pd(acac)_2$ (5)	30	PhMe	24	100	23[c] (17:1)	75
8	**1**	$Pd(acac)_2$ (5)	30	MeCN	24	100	99[c] (5:1)	0
9	**1**	$Pd(acac)_2$ (2)	15	CH_2Cl_2	25	55	55[c]	0
					50	78	75[c] (8:1)	0
							6+**7** (**6**/**7**)	
10	**2**	$Pd(acac)_2$ (2)	30	THF	25	93	90 (3:1)	—
11	**2**	$Pd(acac)_2$ (2)	30	CH_2Cl_2	50	91	90 (3:1)	—

[a] Reaction conditions: 3.5 mmol of aldose; $2PPh_3$/Pd; 4 mL of solvent, 75 °C.
[b] Isolated yields.
[c] ^{13}C NMR determination. Concerning the **3α/β** ratio, its value was higher than 6:1 under all conditions employed.
[d] 1 instead of 3.5 mmol of **1**.
[e] Not determined.

greatly increased at low sugar concentration in THF (entry 6), once again exhibiting the crucial influence of the sugar concentration on the evolution of the reaction.[7,8] In toluene, the sugar was entirely transformed, affording however, lactone **5** as the major product (entry 7). Finally, the use of acetonitrile and dichloromethane gave the telomers with an excellent selectivity (entries 8 and 9) and with no detected lactone formation. Starting from 2,3,4,6-tetra-*O*-benzylglucopyranose (**2**), the telomerization was highly efficient in THF and in CH_2Cl_2, **6** and **7** being isolated in high yields (entries 10 and 11). Under these conditions, no oxidation to the corresponding lactone was observed, which may be due to the low rate of such a reaction compared to the rate of oxidation of furanose sugars.[9]

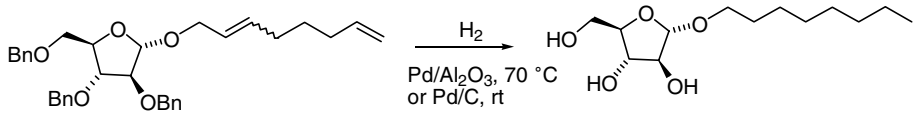
As in our previous studies, the GC–MS analysis of the reaction products revealed the formation of complicated mixtures of isomeric compounds in addition to oligomeric butadiene derivatives. Separation by flash chromatography allowed the isolation of the groups of linear and branched telomers having the α- or β-configuration at the octadienyl chain. Their structures were unambiguously established by ^1H and ^{13}C NMR spectroscopy.

For the arabinosides, the linear α-anomers (**3α**) were the major products exhibiting a *Z*/*E*-double bond distribution of about 1:8, whatever be the experimental conditions used. The linear β-anomers were detected in lower quantities (<15%). The branched isomers were also observed in significant amounts under all conditions employed, **4α** being the major compound in the form of two epimers (at the C′-3 stereocentre of the chain). The ratio of linear to branched telomers highly depends on the solvent used (entries 4 and 7–9). The highest **3**/**4** ratio (17:1) was attained in PhMe but to the detriment of telomer/lactone selectivity. A fair **3**/**4** ratio (8:1) and a high telomer selectivity were obtained in CH_2Cl_2 (entry 9). Comparison with the other arabi-

nose substrates showed that the telomerization reaction reactivity was in the order: free sugar > triacetylated arabinose ≫ tribenzylated arabinose.

2,3,4,6-Tetra-*O*-benzyl-D-glucopyranose (**2**), which was slightly more reactive than the arabinose derivative (compare entries 5 and 10 or 9 and 11) also led mainly to the linear telomers (**6**/**7** = 3:1), the β-anomers being preponderant.

The feasibility of these telomerization reactions having been demonstrated starting from benzylated sugars, we briefly studied the hydrogenation–deprotection of the resulting telomers using **3α** as a model compound (Eq. 1). That would allow their transformation into useful and stable surfactants.[10]



3α **8α** (1)

Using 5% Pd/Al_2O_3 as the catalyst, in cyclohexane at 70 °C under 10 atm of hydrogen, the expected saturated compound **8** was obtained in up to 82% yield, but the reproducibility of these experiments was tedious, as the benzyl groups were not always entirely removed. With 10% Pd/C as the catalyst, the hydrogenation proceeded smoothly in methanol, even at room temperature and under 1 atm of hydrogen, to afford **8** in a reproducible 90–92% yield. These conditions were successfully applied to the hydrogenation/deprotection of a mixture of telomers of arabinofuranoside **3**+**4** or glucopyranoside **6**+**7**.

In conclusion, we have shown that O-benzylated hemiacetal sugars can be used as telogens in palladium-catalyzed butadiene telomerization reaction. Their transformation into non-protected glycosides can be easily achieved *via* a one-pot hydrogenation/deprotection reaction under mild conditions. These benzyl derivatives are less reactive than the corresponding O-acetylated compounds or the free sugars and for practical applications, starting from the free sugar is usually a better option.[6,7] In order to decrease the number of isomers formed, especially the tautomeric sugar forms, the acetylated sugars with a free anomeric hydroxyl are the best starting material.[8]

1. Experimental

1.1. Materials and methods

All experiments were carried out in a 50 mL stainless steel autoclave from Parr Instrument Company. ^1H NMR and ^{13}C NMR were recorded on a Bruker AC500 spectrometer (^1H, 500 MHz; ^{13}C, 125.7 MHz). Signal assignment was based on 2D NMR experiments (COSY, HMQC). The assignment of α-/β-isomers was made by comparison with the spectroscopic data from the methyl glycosides.[11] Elemental analyses were carried out with a Perkin–Elmer CHN 2400 instrument. GC analyses were carried out using a Hewlett–Packard HP-6890 gas chromatograph, fitted with a DB-1 capillary column (25 m, 0.32 mm), a flame ionization detector and an HP-3395 integrator. GC–MS spectra were obtained on a Finigan Trace GC 2000 Series Thermoquest spectrometer, fitted with a DB-1 capillary column (25 m, 0.32 mm).

2,3,5-Tri-*O*-benzyl-β-D-arabinofuranose (**1**), 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**2**) were from Sigma; $Pd(acac)_2$, triphenylphosphane and 5% Pd/Al_2O_3 were purchased from Acros Chemical. 10% Pd/C was purchased from Johnson-Matthey. All chemicals were used as received. Solvents were distilled under argon: DMF from CaH_2, THF from sodium/benzophenone-ketyl, CH_2Cl_2 from P_2O_5. All solvents, after drying, were stored on molecular sieves (4 Å), under an inert atmosphere. 1,3-Butadiene was flash distilled prior to use.

1.2. Typical telomerization procedure (arabinofuranose 1, entry 1)

$Pd(acac)_2$ (21 mg, 0.07 mmol) and triphenylphosphane (36 mg, 0.14 mmol) were charged into a 50 mL stainless steel Parr autoclave. The autoclave was evacuated and filled with argon three times. A DMF soln of O-benzylated carbohydrate (**1**) (1.47 g, 3.5 mmol) was transferred under argon from a Schlenk tube into the autoclave. Gaseous 1,3-butadiene (4.6 mL, 52.5 mmol) was condensed into a cooled Schlenk tube and then transferred into the cooled autoclave. After closing, the autoclave was placed in an oil bath at the required temperature. Stirring was started and continued for 2 h. After cooling, the remaining butadiene was condensed in a Schlenk tube. The conversion was determined by NMR. The ratio of isomeric products was determined by NMR and GC. Separation of the reaction mixture by flash chromatography (SiO_2, 7:3 petroleum ether–EtOAc) gave a telomers fraction (407 mg, 22% as a colourless oil), lactone **5** (176 mg, 12% as a white solid) and starting arabinofuranose **1** (911 mg, 62%).

The other telomerization experiments were carried out under the same conditions, using reagent quantities and reaction times given in Table 1.

The purity of the obtained samples for NMR studies were as follows: (***E***)-**3α** ≈ 95%; (***Z***)-**3α** ≈ 60% (a mixture with the minor epimer **4β**); (***E***)-**3β** ≈ 95%; the major epimer **4β** ≈ 95%; the minor epimer **4β** ≈ 40% (a mixture with (***Z***)-**3α**); (***E***)-**6β** ≈ 95%; (***Z***)-**6β** and epimer **B 7β** as a 1/1 mixture; (***E***)-**6α** ≈ 85% (a mixture with (***E***)-**6β**); epimer **A 7β** ≈ 95%.

1.2.1. Octa-2′,7′-dien-1′-yl 2,3,5-tri-*O*-benzyl-α-D-arabinofuranoside (3α). *(E)-Isomer*: ^{1}H NMR ($CDCl_3$): 7.18–7.40 (m, 15H, OCH_2*Ph*), 5.76 (ddt, *J* 17.0, 10.3, 7.5 Hz, 1H, H-7′), 5.68 (dt, *J* 15.4, 7.0 Hz, 1H, H-3′), 5.53 (dt, *J* 15.4, 7.0 Hz, 1H, H-2′), 5.08 (s, 1H, H-1), 4.97 (d, *J* 17.0 Hz, 1H, H-8′), 4.91 (d, *J* 10.2 Hz, 1H, H-8′), 4.54, 4.49 (AB, *J* 12.0 Hz, 2H, OCH_2Ph), 4.52, 4.45 (AB, *J* 12.0 Hz, 2H, OCH_2Ph), 4.50, 4.43 (AB, *J* 11.8 Hz, 2H, OCH_2Ph), 4.20 (ddd, *J* 7.0, 5.3, 3.7 Hz, 1H, H-4), 4.16 (dd, *J* 11.6, 7.0 Hz, 1H, H-1′), 4.02 (d, *J* 3.1 Hz, 1H, H-2), 3.92 (dd, *J* 11.7, 7.0 Hz, 1H, H-1′), 3.90 (dd, *J* 7.0, 3.1 Hz, 1H, H-3), 3.61 (dd, *J* 10.7, 3.7 Hz, 1H, H-5), 356 (dd, *J* 10.7, 5.3 Hz, 1H, H-5), 1.98–2.10 (m, 4H, H-4′, H-6′), 1.47 (qui, *J* 7.5 Hz, 2H, H-5′).

^{13}C NMR ($CDCl_3$): 138.42 (C-7′), 138.06, 137.86, 137.55 (OCH_2*Ph*), 134.55 (C-3′), 127.36, 127.27, 126.83, 126.77, 126.71, 126.64, 126.53 (OCH_2*Ph*), 125.87 (C-2′), 114.52 (C-8′), 104.82 (C-1), 88.20 (C-2), 83.35 (C-3), 80.45 (C-4), 73.19 (O*C*H_2Ph), 71.90 (O*C*H_2Ph), 71.71 (O*C*H_2Ph), 69.97 (C-1′), 67.72 (C-5), 33.34 (C-6′), 31.52 (C-4′), 28.12 (C-5′).

(Z)-Isomer: ^{1}H NMR ($CDCl_3$): 7.18–7.45 (m, 15H, OCH_2*Ph*), 5.84 (m, 1H, H-7′), 5.63 (m, 2H, H-2′, H-3′), 5.14 (s, 1H, H-1), 5.05 (d, *J* 17.0 Hz, 1H, H-8′), 4.99 (d, *J* 10.5 Hz, 1H, H-8′), 4.61, 4.55 (AB, *J* 12.0 Hz, 2H, OCH_2Ph), 4.60, 4.53 (AB, *J* 12.0 Hz, 2H, OCH_2Ph), 4.59, 4.52 (AB, *J* 11.8 Hz, 2H, OCH_2Ph), 4.30 (dd, *J* 12.0, 6.0 Hz, 1H, H-1′), 4.29 (m, 1H, H-4), 4.13 (dd, *J* 12.0, 6.0 Hz, 1H, H-1′), 4.06 (d, *J* 3.1 Hz, 1H, H-2), 3.97 (dd, *J* 7.6, 3.1 Hz, 1H, H-3), 3.69 (dd, *J* 10.8, 3.7 Hz, 1H, H-5), 3.63 (dd, *J* 10.8, 5.0 Hz, 1H, H-5), 2.08–2.18 (m, 4H, H-4′, H-6′), 1.47 (qui, *J* 7.5 Hz, 2H, H-5′).

^{13}C NMR ($CDCl_3$): 139.02 (C-7′), 138.55, 137.86, 137.06 (OCH_2*Ph*), 133.05 (C-2′), 128.26, 128.18, 127.71, 127.68, 127.62, 127.54, 127.44, 127.38 (OCH_2*Ph*), 125.87 (C-2′), 114.91 (C-8′), 105.13 (C-1), 88.26 (C-2), 83.54 (C-3), 79.48 (C-4), 73.15 (O*C*H_2Ph), 71.90 (O*C*H_2Ph), 71.76 (O*C*H_2Ph), 69.71 (C-5), 62.21 (C-1′), 33.70 (C-6′), 28.55 (C-5′), 26.45 (C-4′).

1.2.2. Octa-2′,7′-dien-1′-yl 2,3,5-tri-*O*-benzyl-β-D-arabinofuranoside (3β). *(E)-Isomer*: ^{1}H NMR (CD_3OD): 7.23–7.70 (m, 15H, OCH_2*Ph*), 5.79 (m, 1H, H-7′), 5.65 (dt, *J* 14.3, 7.7 Hz, 1H, H-3′), 5.47 (dt, *J* 15.3, 6.9 Hz, 1H, H-2′), 4.98 (dm, *J* 17.0, 2.0 Hz, 1H, H-8′), 4.93 (dm, *J* 9.6, 1.5 Hz, 1H, H-8′), 4.93 (s, 1H, H-1), 4.61, 4.57 (AB, *J* 11.8 Hz, 2H, OCH_2Ph), 4.57, 4.53 (AB, *J* 12.1 Hz, 2H, OCH_2Ph), 4.52, 4.50 (AB, *J* 12.0 Hz, 2H, OCH_2Ph), 4.03–4.04 (m, 4H, H-2, H-3, H-4, H-1′), 3.84 (dd, *J* 11.2, 6.9 Hz, 1H, H-1′), 3.51 (d, *J* 10.2 Hz, 1H, H-5), 3.49 (d, *J* 10.2 Hz, 1H, H-5), 1.94–2.10 (m, 4H, H-4′, H-6′), 1.44 (qui, *J* 7.5 Hz, 2H, H-5′).

^{13}C NMR (CD_3OD): 140.14 (C-7′), 139.97, 139.89, 139.58 (OCH_2*Ph*), 136.05 (C-3′), 129.81, 129.50, 129.39, 129.21, 129.15, 129.10 (OCH_2*Ph*), 127.69 (C-2′), 115.62 (C-8′), 101.07 (C-1), 86.02 (C-4), 84.65 (C-2), 81.97 (C-3), 74.01 (C-5), 77.65 (O*C*H_2Ph), 73.86 (O*C*H_2Ph), 73.35 (O*C*H_2Ph), 69.40 (C-1′), 34.72 (C-6′), 33.12 (C-4′), 29.95 (C-5′).

1.2.3. Octa-1′,7′-dien-3′-yl 2,3,5-tri-*O*-benzyl-α-D-arabinofuranoside (4α). *Major epimer*: ^{1}H NMR ($CDCl_3$): 7.12–7.35 (m, 15H, OCH_2*Ph*), 5.76 (ddt, *J* 17.0, 10.2, 6.6 Hz, 1H, H-7′), 5.64 (ddd, *J* 16.9, 10.7, 7.4 Hz, 1H, H-2′), 5.21 (d, *J* 10.7 Hz, 1H, H-1′), 5.20 (d, *J* 16.9 Hz, 1H, H-1′), 5.05 (s, 1H, H-1), 4.97 (d, *J* 17.0 Hz, 1H, H-8′), 4.92 (d, *J* 10.2 Hz, 1H, H-8′), 4.52, 4.50 (AB, *J* 12.0 Hz, 2H, OCH_2Ph), 4.51, 4.47 (AB, *J* 11.5 Hz, 2H, OCH_2Ph), 4.47, 4.42 (AB, *J* 11.1 Hz, 2H, OCH_2Ph), 4.13 (m, 1H, H-4), 4.07 (qui, *J* 7.0 Hz, 1H, H-3′), 3.95 (d, *J* 3.0 Hz, 1H, H-2), 3.85 (dd, *J* 6.0, 3.0 Hz, 1H, H-3), 3.60 (dd, *J* 10.7, 4.0 Hz, 1H, H-5), 3.57 (dd, *J* 10.7, 6.0 Hz, 1H, H-5), 1.96–2.06 (m, 2H, H-6′), 1.40–1.50 (m, 2H, H-4′), 1.38–1.48 (m, 2H, H-5′).

^{13}C NMR ($CDCl_3$): 141.24 (C-2′), 139.47, 139.26, 139.01 (OCH_2*Ph*), 139.74 (C-7′), 129.45, 129.39, 129.20, 129.03, 128.98, 128.93, 128.81, 128.72 (OCH_2*Ph*), 118.61 (C-1′), 115.57 (C-8′), 104.62 (C-1), 89.66 (C-2), 85.51 (C-3), 82.74 (C-4), 78.37 (C-3′), 74.75 (O*C*H_2Ph), 73.36 (O*C*H_2Ph), 73.30 (O*C*H_2Ph), 71.48 (C-5), 36.39 (C-4′), 34.94 (C-6′), 26.27 (C-5′).

Minor epimer: ^{1}H NMR ($CDCl_3$): 7.12–7.35 (m, 15H, OCH_2*Ph*), 5.89 (ddd, *J* 17.0, 10.5, 6.5 Hz, 1H, H-2′), 5.84 (m, 1H, H-7′), 5.28 (d, *J* 17.2 Hz, 1H, H-1′), 5.14 (d, *J* 10.5 Hz, 1H, H-1′), 5.22 (s, 1H, H-1), 5.04 (d, *J* 17.0 Hz, 1H, H-8′), 4.98 (d, *J* 10.5 Hz, 1H, H-8′), 4.63, 4.57 (AB, *J* 12.0 Hz, 2H, OCH_2Ph), 4.61, 4.55 (AB, *J* 11.5 Hz, 2H, OCH_2Ph), 4.61, 4.52 (AB, *J* 11.1 Hz, 2H, OCH_2Ph), 4.29 (m, 1H, H-4), 4.11 (d, *J* 3.0 Hz, 1H, H-2), 4.10 (qui, *J* 7.1 Hz, 1H, H-3′), 3.99 (dd, *J* 7.8, 3.0 Hz, 1H, H-3), 3.66, 3.64 (AB, *J* 10.7 Hz, 2H, H-5), 2.08–2.16 (m, 2H, H-6′), 1.65–1.71 (m, 1H, H-4′), 1.54–1.62 (m, 1H, H-4′), 1.44–1.56 (m, 2H, H-5′).

^{13}C NMR ($CDCl_3$): 139.32 (C-2′), 139.16, 139.01, 138.55 (OCH_2*Ph*), 138.35 (C-7′), 128.36, 128.07, 127.95, 127.77, 127.71, 126.99, 126.93 (OCH_2*Ph*), 114.98 (C-1′), 114.64 (C-8′), 105.15 (C-1), 89.30 (C-2), 82.93 (C-3), 80.44 (C-4), 77.48 (C-3′), 72.53 (O*C*H_2Ph), 71.55 (O*C*H_2Ph), 71.53 (O*C*H_2Ph), 69.70 (C-5), 34.27 (C-4′), 33.97 (C-6′), 23.91 (C-5′).

1.2.4. Octa-2′,7′-dien-1′-yl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (6β). *(E)-Isomer*: ^{1}H NMR ($CDCl_3$): 7.28–7.42 (m, 18H, OCH_2Ph), 7.15–7.22 (m, 2H, OCH_2Ph), 5.84 (ddt, *J* 16.5, 10.5, 6.5 Hz, 1H, H-7′), 5.79 (dt, *J* 15.4, 6.9 Hz, 1H, H-3′), 5.66 (dt, *J* 15.3, 5.8 Hz, 1H, H-2′), 5.05 (dd, *J* 16.6, 1.5 Hz, 1H, H-8′), 5.02, 4.76 (AB, *J* 10.9 Hz, 2H, OCH_2Ph), 5.01 (br d, *J* 10.5, Hz, 1H, H-8′), 4.98, 4.84 (AB, *J* 11.0 Hz, 2H, OCH_2Ph), 4.87, 4.58 (AB, *J* 10.9 Hz, 2H, OCH_2Ph), 4.67, 4.61 (AB, *J* 12.1 Hz, 2H, OCH_2Ph), 4.43 (dd, *J* 11.5, 5.4 Hz, 1H, H-1′), 4.17 (d, *J* 7.1 Hz, 1H, H-1), 4.15 (dd, *J* 11.5, 6.6 Hz, 1H, H-1′), 3.80 (dd, *J* 10.9, 1.8 Hz, 1H, H-6), 3.74 (dd, *J* 10.9, 4.8 Hz, 1H, H-6), 3.70 (t, *J* 9.5 Hz, 1H, H-3), 3.65 (t, *J* 9.5 Hz, 1H, H-4), 3.50 (ddd, *J* 9.5, 4.8, 1.8 Hz, 1H, H-5), 3.54 (dd, *J* 8.4, 8.0 Hz, 1H, H-2), 1.98–2.15 (m, 4H, H-4′, H-6′), 1.50 (qui, *J* 7.5 Hz, 2H, H-5′).

^{13}C NMR ($CDCl_3$): 139.97, 139.89, 139.07, 139.04, 138.74, 138.67 (OCH_2Ph), 138.50 (C-7′), 134.59 (C-3′), 128.30, 128.27, 128.12, 127.89, 127.82, 127.67, 127.58, 127.53, 127.51 (OCH_2Ph), 125.84 (C-2′), 114.68 (C-8′), 102.41 (C-1), 84.65 (C-3), 82.21 (C-2), 77.81 (C-4), 75.64 (O*C*H$_2$Ph), 74.93 (O*C*H$_2$Ph), 74.75 (C-5), 74.74 (O*C*H$_2$Ph), 73.38 (O*C*H$_2$Ph), 70.15 (C-1′), 68.91 (C-6), 33.13 (C-6′), 31.62 (C-4′), 28.15 (C-5′).

(Z)-Isomer: ^{1}H NMR ($CDCl_3$): 7.25–7.42 (m, 18H, OCH_2Ph), 7.12–7.22 (m, 2H, OCH_2Ph), 5.74 (m, 1H, H-7′), 5.61 (m, 2H, H-2′, H-3′), 5.00 (dd, *J* 17.5 Hz, 1H, H-8′), 4.96, 4.83 (AB, *J* 11.0 Hz, 2H, OCH_2Ph), 4.94 (br d, *J* 10.0 Hz, 1H, H-8′), 4.92, 4.80 (AB, *J* 10.9 Hz, 2H, OCH_2Ph), 4.72, 4.52 (AB, *J* 12.1 Hz, 2H, OCH_2Ph), 4.62, 4.54 (AB, *J* 11.9 Hz, 2H, OCH_2Ph), 4.46 (d, *J* 7.5 Hz, 1H, H-1), 4.43 (dd, *J* 10.5, 4.4 Hz, 1H, H-1′), 4.28 (dd, *J* 10.0, 7.5 Hz, 1H, H-1′), 3.79 (dd, *J* 10.9, 1.8 Hz, 1H, H-6), 3.65 (dd, *J* 10.9, 3.0 Hz, 1H, H-6), 3.61 (t, *J* 8.9 Hz, 1H, H-3), 3.57 (t, *J* 8.9 Hz, 1H, H-4), 3.47 (t, *J* 8.2 Hz, 1H, H-2), 3.41 (dd, *J* 8.4, 2.8 Hz, 1H, H-5), 1.98–2.15 (m, 4H, H-4′, H-6′), 1.52 (qui, *J* 7.5 Hz, 2H, H-5′).

^{13}C NMR ($CDCl_3$): 139.97, 139.89, 139.83, 138.97, 138.95, 138.62 (O*C*H$_2$*Ph*), 138.50 (C-7′), 133.75 (C-3′), 128.83, 128.54, 128.44, 128.39, 128.34, 128.23, 128.08 (O*C*H$_2$*Ph*), 125.65 (C-2′), 115.15 (C-8′), 102.87 (C-1), 85.18 (C-3), 82.63 (C-2), 78.45 (C-4), 76.14 (O*C*H$_2$Ph), 75.56 (O*C*H$_2$Ph), 75.04 (O*C*H$_2$Ph), 74.90 (C-5), 74.18 (O*C*H$_2$Ph), 64.98 (C-1′), 69.35 (C-6), 33.70 (C-6′), 27.45 (C-5′), 24.81 (C-4′).

1.2.5. Octa-2′,7′-dien-1′-yl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (6α). *(E)-Isomer*: ^{1}H NMR ($CDCl_3$): 7.23–7.40 (m, 18H, OCH_2Ph), 7.09–7.15 (m, 2H, OCH_2Ph), 5.84 (ddt, *J* 17.2, 10.5, 6.5 Hz, 1H, H-7′), 5.73 (dt, *J* 15.5, 7.3 Hz, 1H, H-3′), 5.61 (ddd, *J* 15.5, 7.4, 5.6 Hz, 1H, H-2′), 5.04 (dd, *J* 17.2, 1.4 Hz, 1H, H-8′), 5.02, 4.87 (AB, *J* 11.0 Hz, 2H, OCH_2Ph), 4.99 (br d, *J* 10.5 Hz, 1H, H8′), 4.86 (d, *J* 3.6 Hz, 1H, H-1), 4.86, 4.48 (AB, *J* 10.5 Hz, 2H, OCH_2Ph), 4.79, 4.68 (AB, *J* 12.1 Hz, 2H, OCH_2Ph), 4.64, 4.49 (AB, *J* 12.0 Hz, 2H, OCH_2Ph), 4.13 (dd, *J* 12.5, 5.6 Hz, 1H, H-1′), 4.03 (t, *J* 9.5 Hz, 1H, H-3), 3.99 (dd, *J* 12.5, 7.4 Hz, 1H, H-1′), 3.82 (br d, *J* 9.6, Hz, 1H, H-5), 3.75 (dd, *J* 10.5, 3.5 Hz, 1H, H-6), 3.67 (t, *J* 9.8 Hz, 1H, H-4), 3.65 (dd, *J* 10.5, 1.6 Hz, 1H, H-6), 3.60 (dd, *J* 9.5, 3.6 Hz, 1H, H-2), 1.96–2.13 (m, 4H, H-4′, H-6′), 1.50 (qui, *J* 7.5 Hz, 2H, H-5′).

^{13}C NMR ($CDCl_3$): 139.03 (C-7′, OCH_2Ph), 138.75, 138.70, 138.41 (OCH_2Ph), 136.05 (C-3′), 128.87, 128.84, 128.57, 128.45, 128.23, 128.17, 128.05 (OCH_2Ph), 126.02 (C-2′), 115.18 (C-8′), 95.68 (C-1), 82.67 (C-3), 80.25 (C-2), 78.20 (C-4), 76.23 (O*C*H$_2$Ph), 75.56 (O*C*H$_2$Ph), 73.94 (O*C*H$_2$Ph), 73.61 (O*C*H$_2$Ph), 70.62 (C-5), 68.92 (C-6), 68.29 (C-1′), 33.75 (C-6′), 32.20 (C-4′), 28.69 (C-5′).

1.2.6. Octa-1′,7′-dien-3′-yl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (7β) (two epimers A and B, 1:1). *Epimer* **A**: ^{1}H NMR ($CDCl_3$): 7.29–7.50 (m, 18H, OCH_2Ph), 7.12–7.21 (m, 2H, OCH_2Ph), 5.91 (ddd, *J* 17.2, 10.5, 6.5 Hz, 1H, H-2′), 5.74 (m, 1H, H-7′), 5.20 (d, *J* 17.0 Hz, 1H, H-1′), 5.10 (d, *J* 10.4 Hz, 1H, H-1′), 4.99 (d, *J* 17.2 Hz, 1H, H-8′), 4.96 (d, *J* 9.8 Hz, 1H, H-8′), 4.96, 4.74 (AB, *J* 10.2 Hz, 2H, OCH_2Ph), 4.95, 4.79 (AB, *J* 10.4 Hz, 2H, OCH_2Ph), 4.82, 4.54 (AB, *J* 11.1 Hz, 2H, OCH_2Ph), 4.62, 4.56 (AB, *J* 11.5 Hz, 2H, OCH_2Ph), 4.45 (d, *J* 8.2 Hz, 1H, H1), 4.10 (qui, *J* 7.2 Hz, 1H, H-3′), 3.73 (dd, *J* 10.9, 1.8 Hz, 1H, H-6), 3.68 (dd, *J* 10.7, 3.5 Hz, 1H, H-6), 3.64 (t, *J* 9.0 Hz, 1H, H-3), 3.58 (t, *J* 9.5 Hz, 1H, H-4), 3.47 (t, *J* 8.4 Hz, 1H, H-2), 3.42 (ddd, *J* 9.5, 4.8, 1.5 Hz, 1H, H-5), 2.06–2.15 (m, 2H, H-6′), 1.65–1.75 (m, 1H, H-4′), 1.47–1.65 (m, 1H, H-4′), 1.52 (qui, *J* 7.5 Hz, 2H, H-5′).

^{13}C NMR ($CDCl_3$): 139.83 (OCH_2Ph), 139.15 (C-2′), 138.97, 138.95, 138.62 (OCH_2Ph), 138.64 (C-7′), 128.83, 128.54, 128.44, 128.39, 128.34, 128.23, 128.08 (OCH_2Ph), 116.31 (C-1′), 115.21 (C-8′), 102.95 (C-1), 85.40 (C-3), 82.45 (C-3′), 82.89 (C-2), 78.05 (C-4), 76.19 (O*C*H$_2$Ph), 75.45 (O*C*H$_2$Ph), 75.30 (O*C*H$_2$Ph), 74.95 (C-5), 73.94 (O*C*H$_2$Ph), 69.47 (C-6), 34.81 (C-4′), 34.17 (C-6′), 24.81 (C-5′).

Epimer **B**: ^{1}H NMR ($CDCl_3$): 7.22–7.35 (m, 18H, OCH_2Ph), 7.15–7.20 (m, 2H, OCH_2Ph), 5.80 (ddd, *J* 17.6, 10.5, 8.5 Hz, 1H, H-7′), 5.67 (ddd, *J* 17.0, 10.5, 6.4 Hz, 1H, H-2′), 5.23 (d, *J* 17.0 Hz, 1H, H-1′), 5.21 (d, *J* 10.5 Hz, 1H, H-1′), 5.00 (d, *J* 17.2 Hz, 1H, H-8′), 4.98, 4.81 (AB, *J* 11.0 Hz, 2H, OCH_2Ph), 4.94 (d, *J* 9.8 Hz, 1H, H-8′), 4.90, 4.77 (AB, *J* 10.2 Hz, 2H, OCH_2Ph), 4.71, 4.53 (AB, *J* 10.9 Hz, 2H, OCH_2Ph), 4.62, 4.55 (AB, *J* 12.2 Hz, 2H, OCH_2Ph), 4.47 (d, *J* 7.8 Hz, 1H, H-1), 4.23 (qui, *J* 6.4 Hz, 1H, H-3′), 3.72 (d, *J* 10.3, Hz, 1H, H-6), 3.66 (dd, *J* 10.3, 2.8 Hz, 1H, H-6), 3.62 (t, *J* 8.9 Hz, 1H, H-3), 3.58 (t, *J* 8.9 Hz, 1H,

H-4), 3.46 (t, *J* 8.1 Hz, 1H, H-2), 3.41 (dd, *J* 8.4, 2.8 Hz, 1H, H-5), 2.04–2.14 (m, 2H, H-6′), 1.65–1.75 (m, 1H, H-4′), 1.47–1.65 (m, 1H, H-4′), 1.49 (qui, *J* 7.5 Hz, 2H, H-5′).

^{13}C NMR ($CDCl_3$): 139.43 (OCH_2*Ph*), 138.70 (C-7′), 138.37, 138.25, 138.12 (OCH_2*Ph*), 137.78 (C-2′), 128.31 (OCH_2*Ph*), 128.29, 128.21, 127.90, 127.80, 127.66, 127.63, 127.59, 127.51 (OCH_2*Ph*), 118.12 (C-1′), 114.54 (C-8′), 99.89 (C-1), 84.81 (C-3), 82.10 (C-2), 78.64 (C3′), 77.89 (C-4), 75.63 (O*C*H_2Ph), 74.88 (O*C*H_2Ph), 74.78 (O*C*H_2Ph), 74.68 (C-5), 73.37 (O*C*H_2Ph), 68.93 (C-6), 34.33 (C-4′), 33.57 (C-6′), 24.28 (C-5′).

1.2.7. (*Z*)-Octa-2,7-dien-1-yl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (6α) and octa-1′,7′-dien-3′-yl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (7α). The compounds (two epimers 1:1) were obtained as an inseparable mixture with (*E*)-(**6α**) and (*E*)-(**6β**) 1:1:1:4:5. Their structures were tentatively assigned in accord with ^{13}C NMR characteristic signals: 96.56, 96.08, 93.86 (C-1); 80.63, 80.24, 80.00 (C-2, O*C*H), 78.25, 77.71 (C-4, O*C*H), 63.14 (O*C*H_2).

1.3. Hydrogenation over Pd/Al_2O_3

Octa-2,7-dien-1-yl 2,3,4-tri-*O*-benzyl-α-D-arabinofuranoside (**3α**) (352 mg, 0.67 mmol) was dissolved in 4 mL of cyclohexane and transferred into 50 mL stainless steel autoclave, which had been charged with 211 mg (60 %) of Pd/Al_2O_3 (5%) under Ar. The autoclave was pressurized with hydrogen to 10 bar and heated to 70 °C with stirring. After 8 h, residual hydrogen was flushed. The solvent was evaporated and oct-1′-yl α-D-arabinofuranoside (**8α**) was purified by flash chromatography on SiO_2 (95:5 CH_2Cl_2–MeOH). Yield 144 mg (82%); colourless oil. ^{13}C NMR ($CDCl_3$): 107.97 (C-1), 85.17, 80.99, 77.56 (C-2, C-3, C-4), 68.35 (C-1′), 68.66 (C-4), 61.54 (C-5), 32.21, 29.88, 29.78, 29.65, 27.78, 23.02 (C-2′, C-3′, C-4′, C-5′, C-6′ and C-7′), 14.45 (C-8′).

1.4. General hydrogenation procedure over 10% Pd/C

To a soln of O-benzylated glycoside (2 mmol) in 15 mL of MeOH was added 0.1 equiv of 10% Pd/C. The reaction mixture was stirred under 1 atm of hydrogen pressure for 12 h at room temperature. The solvent was evaporated and the product purified by flash chromatography (19:1 CH_2Cl_2–MeOH).

1.4.1. Oct-1′-yl α-D-arabinofuranoside (8α). Colourless oil (499 mg, 92%) from 1.09 g (2.06 mmol) of **3α**.

1.4.2. Mixture of oct-1′-yl (8α/β) and oct-3′-yl D-arabinofuranosides. Colourless oil (211 mg, 97%) from a mixture of D-arabinofuranosides **3α/β** and **4α** (610 mg; **3α/3β/4α** (as 2 epimers): 1:1:1).

No signal of a double bond and a benzyl group were observed in ^{13}C NMR of the reaction mixture confirming the absence of double bond or benzyl group. A mixture of four octyl glycosides obtained by flash chromatography was analyzed using ^{13}C NMR spectroscopy and GC–MS: ^{13}C NMR: *oct-1′-yl* β-D-*arabinofuranoside* (**8β**)*:* ^{13}C NMR ($CDCl_3$): 107.97 (C-1), 85.17, 80.99, 77.56 (C-2, C-3, C-4), 68.35 (C-1′), 68.66 (C-4), 61.54 (C-5), 31.86, 29.78, 26.92, 26.15, 23.75, 29.35 (C-2′, C-3′, C-4′, C-5′, C-6′ and C-7′), 14.20 (C-8′). *Oct-1′-yl* α-D-*arabinofuranoside* (**8α**) was in accord with that described above.

The signals 106.93, 106.61, 86.07, 79.85, 79.12, 78.41, 60.58, 33.96, 33.12, 28.92, 26.03, 25.95, 23.16, 21.69, 9.96, 9.21 were attributed to *oct-3′-yl* D-*arabinofuranosides* (two epimers).

GC–MS: To obtain an adequate GC–MS response, the acetylation of a sample (0.1 g) by acetic anhydride (0.2 mL) in the presence of pyridine (0.05 mL) was performed. The signals of four isomers were observed ($\tau = 15.65$, 15.80 min (branched isomers); 17.72, 17.77 min (linear isomers)).

$\tau = 15.65$ min: CIMS *m*/*z* 406 (27, M+18$^+$), 259 (100), 174 (6), 146 (28), 98 (53), 77 (93). $\tau = 15.80$ min: CIMS *m*/*z* 406 (25, M+18$^+$), 259 (86), 174 (8), 146 (29), 98 (57), 77 (100). $\tau = 17.72$–17.77 min: CIMS *m*/*z* 406 (60, M+18$^+$), 259 (100), 174 (5), 98 (25), 77 (30).

1.4.3. Oct-1′-yl D-glucopyranoside (α/β 1:4). Colourless oil (288 mg, 97%) from 662 mg (1.02 mmol) of octa-2,7-dien-1-yl 2,3,4,6-tetra-*O*-benzyl-D-glucopyranoside **(6)** (α/β 1:4) in EtOH using the same procedure. The ^{1}H and ^{13}C NMR spectra of the products were in accord with those reported in the literature.[12]

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